

# Electronic Structure of Large-Scale Graphene Nanoflakes

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With the help of the recently developed SIESTA-PEXSI method [J. Phys.: Condens. Matter **26**, 305503 (2014)], we perform Kohn-Sham density functional theory (DFT) calculations to study the stability and electronic structure of hexagonal graphene nanoflakes (GNFs) with up to 11,700 atoms. We find the electronic properties of GNFs, including their cohesive energy, HOMO-LUMO energy gap, edge states and aromaticity, depend sensitively on the type of edges (ACGNFs and ZZGNFs), size and the number of electrons. We observe that, due to the edge-induced strain effect in ACGNFs, large-scale ACGNFs' cohesive energy decreases as their size increases. This trend does not hold for ZZGNFs due to the presence of many edge states in ZZGNFs. We find that the energy gaps  $E_g$  of GNFs all decay with respect to  $1/L$ , where  $L$  is the size of the GNF, in a linear fashion. But as their size increases, ZZGNFs exhibit more localized edge states. We believe the presence of these states makes their gap decrease more rapidly. In particular, when  $L$  is larger than 6.40 nm, we find that ZZGNFs exhibit metallic characteristics. Furthermore, we find that the aromatic structures of GNFs appear to depend only on whether the system has  $4N$  or  $4N+2$  electrons, where  $N$  is an integer.

## I. INTRODUCTION

Graphene, a two-dimensional (2D)  $sp^2$ -hybridized carbon sheet, has recently received considerable interest owing to its outstanding properties [1–3], such as its high carrier mobility, which is important for graphene-based electronic devices, such as field effect transistors (FETs). However, electronic devices fabricated from graphene typically show a small on-off ratio due to its zero bandgap. Therefore, many bandgap engineering techniques have been developed both experimentally and theoretically to open a small band gap in graphene [4–6]. One of these techniques involves cutting 2D graphene into finite-sized one-dimensional (1D) graphene nanoribbons (GNRs) [7–17] and zero-dimensional (0D) graphene nanoflakes (GNFs) [18–25]. Theoretically, significant efforts [12–17] based on first-principles calculations have been made to characterize properties of GNRs with respect to the atomic configuration of their edges, which are of either the armchair (AC) or zigzag (ZZ) types. These properties can be used to guide bandgap engineering in 1D GNRs for graphene-based electronic devices.

In this study, we focus on 0D GNFs, which are also known as graphene quantum dots [26]. Experimentally, GNFs have been studied due to their unique properties and potential applications [27–30]. In particular, for large GNFs with lateral dimensions up to 20 nm, the de-

pendency of the electronic structure on the size and edge type was demonstrated by experiments [20]. It has been shown that ZZGNFs exhibit metallic features and have localized edge states.

Theoretically, the structural and electronic properties of small GNFs with up to hundreds of atoms have been studied with first-principles calculations [21–25]. The stability and the HOMO-LUMO energy gaps have been calculated. However, for large GNFs, theoretical studies have been limited. Most of the studies are based on the Hückel theory [31], pseudo- $\pi$  method [32] or tight-binding method [33, 34]. This limitation is mainly due to the lack of computational tools that can be used to perform large-scale first-principles calculations that involve thousand or tens of thousands of atoms.

The hexagonal arrangement of carbon atoms in GNFs suggests that they may share similar properties with other graphene based aromatic compounds such as polycyclic aromatic hydrocarbons (PAHs) [35–37], carbon nanotubes (CNTs) [38–40] and GNRs [41–43], whose electronic structures can be characterized by their Kekulé bonding structures, which contain alternating single and double bonds within a hexagonal system such as those found in a benzene molecule shown in Fig. 1(a). For benzene, there are two different Kekulé structures that are distinguished by the locations of single and double bonds. The resonance of these two complementary structures results in what is known as a Clar sextet [44, 45]. For some polycyclic aromatic compounds such as graphene, Clar sextets can appear at several possible locations. It follows from Clar's theory that these sextets are disjoint and separated by Kekulé structures. Different but equivalent Clar's formulas can be derived based on the positions of

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the sextets. For example, Fig. 1(b) shows three Clar's formula for a graphene [42]. However, it is not clear whether Clar's theory remains valid for large GNFs. First principle calculations based density functional theory may be used to answer this question.

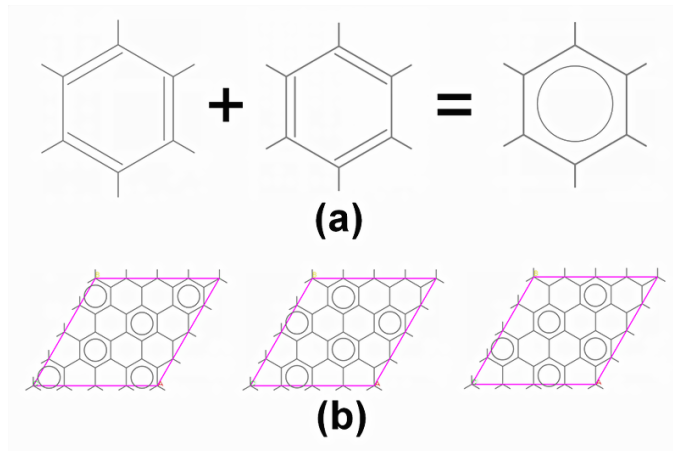


FIG. 1: (Color online) The Kekulé and Clar structure models for (a) benzene and (b) graphene. Doublet and circle denote C=C double bond and benzenoid ring, respectively.

In this paper, we perform large scale first-principle calculations for GNFs systems up to 11,700 atoms, using the recently developed PEXSI method [46–50] implemented in SIESTA [51]. We report the computed cohesive energies and HOMO-LUMO energy gaps for ACGNFs and ZZGNFs. We predict that large ACGNFs are the most stable type of GNFs, thus are easier to form than ZZGNFs in the experiments. The stability of large ACGNFs can be understood by examining edge-induced strain for ACGNFs of different sizes. We find that, as the system size increases, the portion of ACGNF atoms that have small or zero strain also increases. This trend renders large ACGNFs more stable than small ACGNFs. We find that the HOMO-LUMO energy gap (denoted by  $E_g$ ) of ACGNFs and ZZGNFs decreases with respect to the system size. Quantitatively, the relationship between  $E_g$  and  $L$  can be described by  $E_g = \alpha/L + \beta$ , where  $L$  is the size of the GNF, and  $\alpha$  and  $\beta$  are some constants. We find that the HOMO-LUMO energy gap associated with ZZGNFs decreases more rapidly than that associated with ACGNFs. We calculate the local density of states (LDOS) and projected density of states (PDOS) associated with the HOMO and LUMO states for both ACGNFs and ZZGNFs. We find that the LDOS of ZZGNFs exhibits features that result from increasingly significant contribution by the edges as the system size increases, while the opposite holds for ACGNFs. By examining the LDOS for the HOMO state, we identify two aromatic structures of ACGNFs with different stability characteristics. In particular, we find that the aromatic structure of ACGNFs depends on whether the system has  $4N$  or  $4N + 2$  electrons ( $N$  is an integer), and the

induced stability character can be interpreted in terms of the competition between Clar's theory for inner structure and the steric effects of boundary structure in organic chemistry.

## II. THEORETICAL MODELS AND METHODS

Both ACGNFs and ZZGNFs we consider have diameters below 20 nm. Each GNF contains either  $4N$  or  $4N+2$  electrons ( $N$  is an integer), and the number of electrons depends on the atomic configuration near the corners of the GNF. For ACGNFs, the chemical formulae associated with these two different types of configurations are  $C_{18n^2-30n+12}H_{12n-12}$  and  $C_{18n^2-18n+6}H_{12n-6}$ , respectively ( $n$  is an integer). All ZZGNFs share similar structures but have different widths. The chemical formula of ZZGNFs with both  $4N$  and  $4N + 2$  electrons can be expressed by the same formula  $C_{6n^2}H_{6n}$  ( $n$  is an integer). First-principle calculations for a number of ACGNFs from  $C_{42}H_{18}$  to  $C_{11400}H_{300}$  and ZZGNFs from  $C_{24}H_{12}$  to  $C_{1014}H_{78}$  are performed in this study. The atomic geometries of some of these ACGNFs and ZZGNFs are shown in Fig 2.

We use the Kohn-Sham DFT based electronic structure analysis implemented in the SIESTA [52] software package to study properties of the GNFs discussed above. When performing DFT calculations for these GNFs, we include 20 Å vacuum space in each of the  $X$ ,  $Y$  and  $Z$  directions, which is sufficiently large for separating the interactions between neighboring slabs. We choose the PBE exchange correlation functional [53], which generally gives a good description of electronic structures of GNRs [42, 43] and GNFs [27, 28]. We use the double zeta plus polarization orbital basis set (DZP) to describe the valence electrons within the framework of a linear combination of numerical atomic orbitals (LCAO) [54]. All atomic coordinates are fully relaxed using the conjugate gradient (CG) algorithm until the energy and force convergence criteria of  $10^{-4}$  eV and  $0.04$  eV/Å respectively are reached. All calculations are performed on the Edison system available at the National Energy Research Scientific Computing (NERSC) center.

Due to the large number of atoms contained in the GNFs under study, the standard diagonalization (DIAGON) method in SIESTA, which is based on the ScaLAPACK [55] software package, becomes prohibitively expensive. Therefore, we use the recently developed pole expansion and selected inversion (PEXSI) technique [51] to reduce the computational time without sacrificing accuracy even for metallic systems. The PEXSI technique allows the evaluation of physical quantities such as electron density, energy, atomic force to be performed without calculating any eigenvalue or eigenfunction. The resulting SIESTA-PEXSI method can be highly scalable to more than 10,000 cores. It can effectively reduce the wall clock time.

To demonstrate the efficiency and accuracy of PEXSI

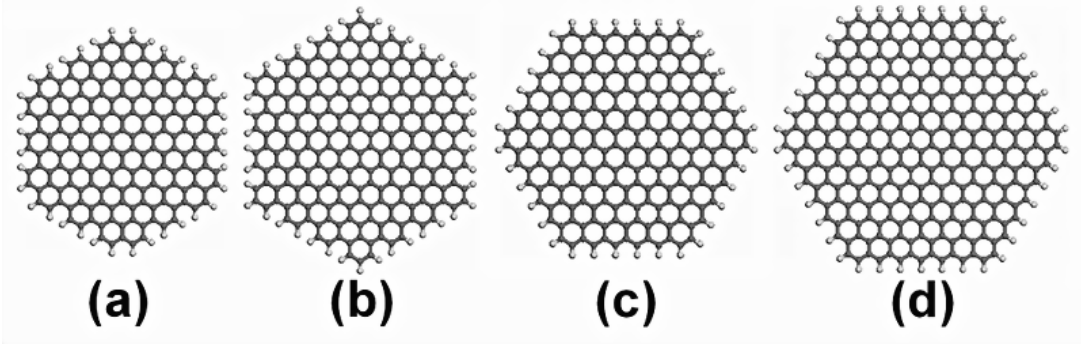


FIG. 2: (Color online) Atomic geometries of ACGNFs and ZZGNFs, (a)  $C_{180}H_{36}$  ( $4N$ ), (b)  $C_{222}H_{42}$  ( $4N+2$ ), (c)  $C_{216}H_{36}$  ( $4N$ ) and (d)  $C_{294}H_{42}$  ( $4N+2$ ). The white and gray balls denote hydrogen and carbon atoms, respectively.

for GNFs here, we measure the average wall clock time spent in each self-consistent field iteration for both PEXSI and diagonalization (DIAGON) methods implemented in SIESTA for  $C_{2382}H_{138}$ . The PEXSI calculation is performed using 40 poles for all systems. We find that the time used by DIAGON is 5 times more than that used by PEXSI when these calculations were performed on 640 cores. The difference of total energy between DIAGON and PEXSI calculations is less than  $10^{-4}$  eV per atom. The accuracy of PEXSI calculation can be further improved by simply increasing the number of poles. The performance gain of PEXSI relative to DIAGON becomes more substantial as the system size increases. This is due to the  $\mathcal{O}(N^{3/2})$  asymptotic complexity of PEXSI for a quasi-2D system consisting of  $N$  atoms, which is superior to the  $\mathcal{O}(N^3)$  complexity of the DIAGON method. Furthermore, the PEXSI method has much higher parallel scalability than the DIAGON method in SIESTA when performed on massively parallel computing platforms (with more than 1000 cores). As an example, we compare the wall clock time required to perform one self-consistent field (SCF) iteration on  $C_{11400}H_{300}$ . We found that the computational time required by DIAGON is 23 times of that used by the PEXSI method in SIESTA when the computation is performed on 2560 cores.

In the SIESTA-PEXSI solver, various types of density of states (DOS) can be evaluated without computing any eigenvalue or eigenfunction as well. The standard DOS allows us to obtain the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The DOS can be computed via a procedure called *inertia counting*, which is based on direct factorization of sparse matrices and is described in detail in [51]. The inertia counting procedure can efficiently provide DOS at arbitrary place along the spectrum with very high resolution, and the DOS near the Fermi energy can be used to identify the energy levels of the HOMO and LUMO state, and therefore the HOMO-LUMO band gap up to the resolution of the DOS. For example, our calculated energy gap of benzene ( $C_6H_6$ ) is 5.25 eV with the PEXSI method, in agreement with the DIAGON method (5.24 eV) in SIESTA.

The spatial distribution of electrons associated with HOMO, LUMO, and other states along the spectrum can be deduced from the local DOS (LDOS), defined as as

$$\rho_L(r, \varepsilon) = 2 \sum_i \delta(\varepsilon - \varepsilon_i) |\psi_i(r)|^2,$$

where  $\psi_i$  is a Kohn-Sham orbital and  $\varepsilon_i$  is the corresponding Kohn-Sham energy. The LDOS  $\rho(r, \varepsilon)$  provides an approximation to the electron density contributed by electron states whose corresponding energies are near  $\varepsilon$ . For instance, large values of LDOS on the edges of a GNF indicates the presence of *edge states*, which are electronic states in which relatively high electron density is found near the edges of the GNF. In the atomic orbital representation,

$$\rho_L(r, \varepsilon) = 2 \sum_i \sum_{\mu, \nu} \varphi_\mu(r) \varphi_\nu(r) \delta(\varepsilon - \varepsilon_i) c_{\mu, i} c_{\nu, i},$$

where  $\mu, \nu$  are atomic orbital indices,  $\varphi_\mu$  is the  $\mu$ th atomic orbital,  $c_{\mu, i}$  is the  $\mu$ th component of the  $i$ th Kohn-Sham eigenvector  $\psi_i$ , and  $H, S$  are the finite dimensional Hamiltonian and the overlap matrix corresponding to the atomic orbitals, respectively. For a given  $\varepsilon$ ,  $\rho_L(r, \varepsilon)$  can be computed efficiently by the PEXSI method without diagonalizing the Kohn-Sham Hamiltonian. The expression used in SIESTA-PEXSI is [51]:

$$\rho_L(r, \varepsilon) \approx \frac{2}{\pi} \sum_{\mu, \nu} \varphi_\mu(r) \varphi_\nu(r) \Im [H - (\varepsilon + i\eta)S]_{\mu, \nu}^{-1},$$

where  $\eta$  is a small broadening parameter describing the resolution of the LDOS, and  $\Im$  denotes the imaginary part. When  $\varepsilon$  is chosen to be near the HOMO and LUMO energy level, the corresponding LDOS provides accurate approximation of the electronic structure of the HOMO and LUMO states.

The projected DOS (PDOS) measures the contribution of  $\mu$ th atomic orbital (hence the atom itself) to the DOS around the energy level  $\varepsilon$ . The definition of the PDOS is

$$g_\mu(\varepsilon) = \frac{2}{N_a} \sum_i \sum_\nu c_{\nu, i} c_{\mu, i} S_{\mu, \nu} \delta(\varepsilon - \varepsilon_i).$$

Similar to the LDOS, the PDOS can be evaluated by the PEXSI technique efficiently using the expression

$$g_{\mu}(\varepsilon) \approx \frac{2}{N_a \pi} \sum_{\nu} S_{\mu,\nu} \text{Im} [H - (\varepsilon + i\eta)S]_{\mu,\nu}^{-1}.$$

Such a procedure avoids the computation of eigenvalues and eigenfunctions of the Kohn-Sham Hamiltonian, and is very efficient for large systems containing thousands of atoms.

### III. RESULTS AND DISCUSSION

In this section, we present computational results obtained from using SIESTA-PEXSI to study properties of GNFs. These properties include the stability, HOMO-LUMO energy gap, the presence of edge states and the aromatic structure.

#### A. Stability

The stability of a GNF can be deduced from its cohesive energy, which is defined as

$$E_c = E_{GNF} - N_C \mu_C - N_H \mu_H,$$

where  $E_{GNF}$  represents the total energy of the GNF,  $\mu_C$  and  $\mu_H$  are the chemical potentials of carbon and hydrogen atoms respectively, and  $N_C$  and  $N_H$  correspond to the number of carbon and hydrogen atoms in the GNF respectively. Fig. 3 shows that the stability of GNFs depends strongly on their sizes and edge types. For small GNFs with up to hundreds of atoms, the cohesive energies of armchair edged GNFs (ACGNFs) and zigzag edged GNFs (ACGNFs) all increase with respect to the number of carbon atoms, which confirms the previous theoretical results [24]. However, the rate of increase is much higher for ZZGNFs than that for ACGNFs.

For large GNFs with thousands of atoms, Fig. 3 shows that the cohesive energies of ACGNFs decrease with respect to the number of carbon atoms. This observation is very different from the trend observed for ZZGNFs, which exhibits a continued increase in cohesive energy as the number of atoms in the system increases. Therefore, we predict that large ACGNFs with thousands of atoms to be thermodynamically more stable and easier to produce experimentally than ZZGNFs. We also observe that large ACGNFs with  $4N$  electrons are slightly more stable than ACGNFs with  $4N+2$  electrons.

The increased stability of large scale ACGNFs can be understood from edge induced bond strain. Edge induced bond strain results from the process of cutting graphene into hexagonal nanoflakes. The carbon atoms in the outer layers of a nanoflake tends to relax and stretch outward once they are cut away from the graphene. For GNRs, the edge-induced strain has an important influence on their electronic properties [42] such as the energy gaps [14]. Here we find that edge-induced strain

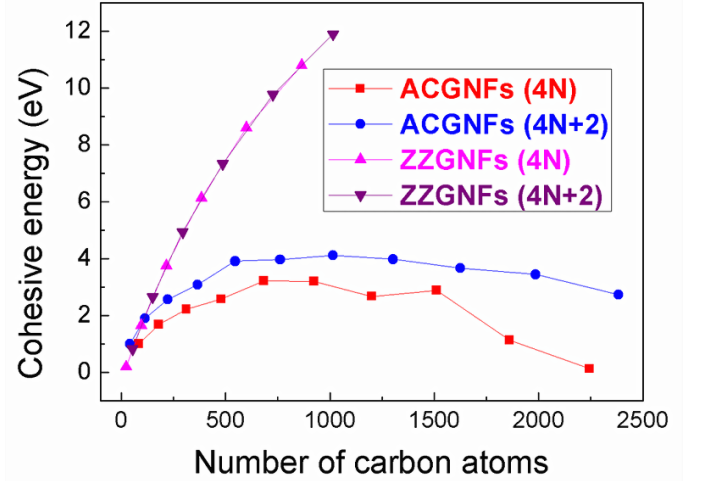


FIG. 3: (Color online) Cohesive energy  $E_c$  (eV) of ACGNFs and ZZGNFs with different total number of electrons ( $4N$  and  $4N+2$ ,  $N$  is an integer) as a function of the number of carbon atoms.

also plays an important role on the stability of ACGNFs. Edge-induced strain of a GNF can be measured by

$$\delta_{C-C} = (L_{GNFs} - L_G)/L_G,$$

where  $L_{GNFs}$  and  $L_G$  represent the equilibrium carbon-carbon bond length in a GNF and in an ideal monolayer of graphene, respectively [14]. The carbon-carbon bond length in an ideal monolayer of graphene is  $L_G = 1.425$  Å [2].

We plot the computed rotationally averaged edge-induced strain associated with carbon atoms in different layers of three ACGNFs ( $C_{180}H_{36}$ ,  $C_{684}H_{72}$  and  $C_{2244}H_{132}$ ) in Fig. 4. The positive strain values indicate that the C=C double bonds inside these ACGNFs are longer than the ideal bond length in a graphene. The increased bond length renders ACGNFs less stable compared to graphene. Furthermore, these carbon-carbon bonds become even longer when they are closer to the edges of ACGNFs. However, as the size of an ACGNF increases, its carbon-carbon bond length becomes shorter. It eventually converges to that of an ideal monolayer graphene. Therefore, the edge-induced strain in an ACGNF is weakened as its size increases. The weakened strain in large ACGNFs (with more than a thousand atoms) makes them more stable compared to small ACGNFs.

#### B. HOMO-LUMO energy gap

Fig. 5 shows how the calculated HOMO-LUMO energy gaps  $E_g$  (eV) change with respect to the diameters  $L$  (nm) of ACGNFs and ZZGNFs, respectively. Our calculations show that the HOMO-LUMO gaps of ACGNFs

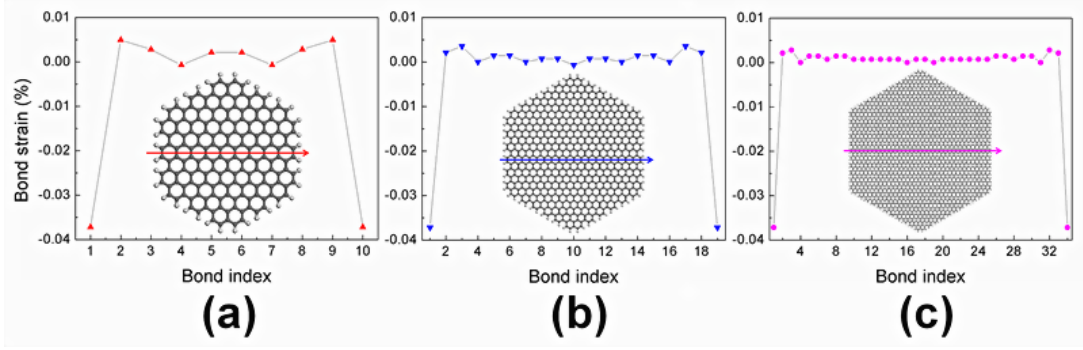


FIG. 4: (Color online) Edge-induced strain of carbon-carbon bonds in ACGNFs, (a)  $C_{180}H_{36}$ , (b)  $C_{684}H_{72}$  and (c)  $C_{2244}H_{132}$ . Carbon-carbon bonds of ACGNFs marked along the arrow direction are considered as shown in the insert.

and ZZGNFs decrease as  $L$  increases. The decrease in  $E_g$  can be attributed to the quantum confinement effect [56–58]. A linear least squares fitting yields  $E_g = 3.37/L$  for ACGNFs and  $E_g = -0.62 + 3.97/L$  for ZZGNFs respectively. These results are close to previous models constructed from experimental measurements ( $E_g = 1.57 \pm 0.21/L^{1.19 \pm 0.15}$ ) [20] obtained from scanning tunneling spectroscopy, and other theoretical predictions ( $E_g = 1.68/L$ ) [2] based on quantum confinement and the linear dispersion analysis of graphene.

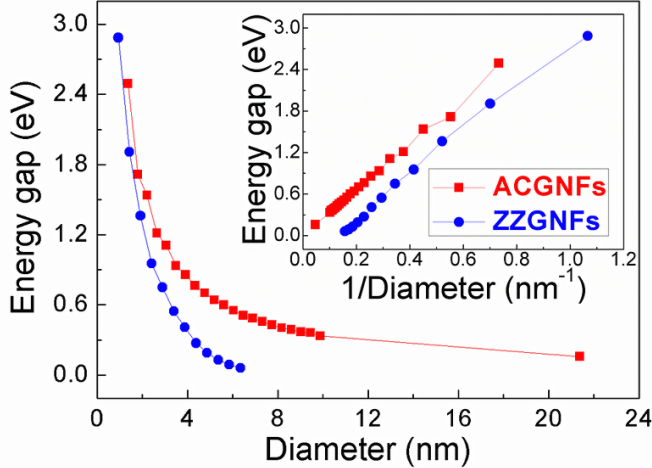


FIG. 5: (Color online) Energy gap  $E_g$  (eV) of ACGNFs and ZZGNFs as a function of sizes  $L$  (nm) (Diameter). Energy gap ( $E_g$ )-size ( $1/L$ ) relation of ACGNFs and ZZGNFs is shown in the insert.

We notice that the HOMO-LUMO energy gap of ZZGNFs decreases more rapidly with respect to  $L$  than that of ACGNFs. This observation is consistent with previous analysis obtained from a tight-binding model [34]. The more rapid decrease in HOMO-LUMO energy gap is likely to be caused by the presence of edge states whose electron densities concentrate near the edges of ZZGNFs. Experimental studies [20] have shown that there are in-

deed many localized edge states concentrating on carbon atoms along the edges of ZZGNFs, whereas no edge state has been detected in ACGNFs.

We also observe that large ZZGNFs with a diameter larger than  $6.40 \text{ nm}$  exhibit metallic features. This is in good agreement with the experimental measurements [20]. On the other hand, ACGNFs are all found to be semiconducting with small energy gaps similar to ACGNRs [13–15]. However, the HOMO-LUMO gap of ACGNFs decreases monotonically as  $L$  increases (i.e.,  $E_g \propto 1/L$ ), whereas the HOMO-LUMO gaps of ACGNRs intricately depends on their widths ( $3N/3N+1/3N+2$ , where  $N$  is an integer) [14]. Therefore, large ACGNFs show higher stability, and their HOMO-LUMO energy gaps can be easily controlled for graphene-based electronic devices.

### C. Edge states

As we discussed earlier, the small HOMO-LUMO gap of a GNF is related to the presence of edge states. Edge states can be revealed by computing local density of states (LDOS). In Figs. 6, 7 and 8, we show isosurfaces of the LDOS overlayed on atomic structures of various GNFs for both  $\epsilon_{\text{HOMO}}$  and  $\epsilon_{\text{LUMO}}$ , where the HOMO and LUMO energies  $\epsilon_{\text{HOMO}}$  and  $\epsilon_{\text{LUMO}}$  are estimated from the DOS.

We observe that for small ACGNFs shown in Fig. 6(a) and (b), the LDOS plots associated with HOMO and LUMO states are not localized in any particular region of the ACGNFs. However, for small ZZGNFs shown in Fig. 6(c) and (d), the LDOS plots associated with the HOMO and LUMO states show high levels of electron density on the edges of these ZZGNFs. This is a clear indication that edge states play an important role.

At the bottom of each subfigure in Fig. 6, we also plot the projected DOS associated with atomic orbitals centered at the hydrogen atoms and different layers of carbon atoms starting from the outermost layer which forms the edge of the GNF. We can see from Fig 6(a) and (b) that carbon atoms in the outer layers and in the center



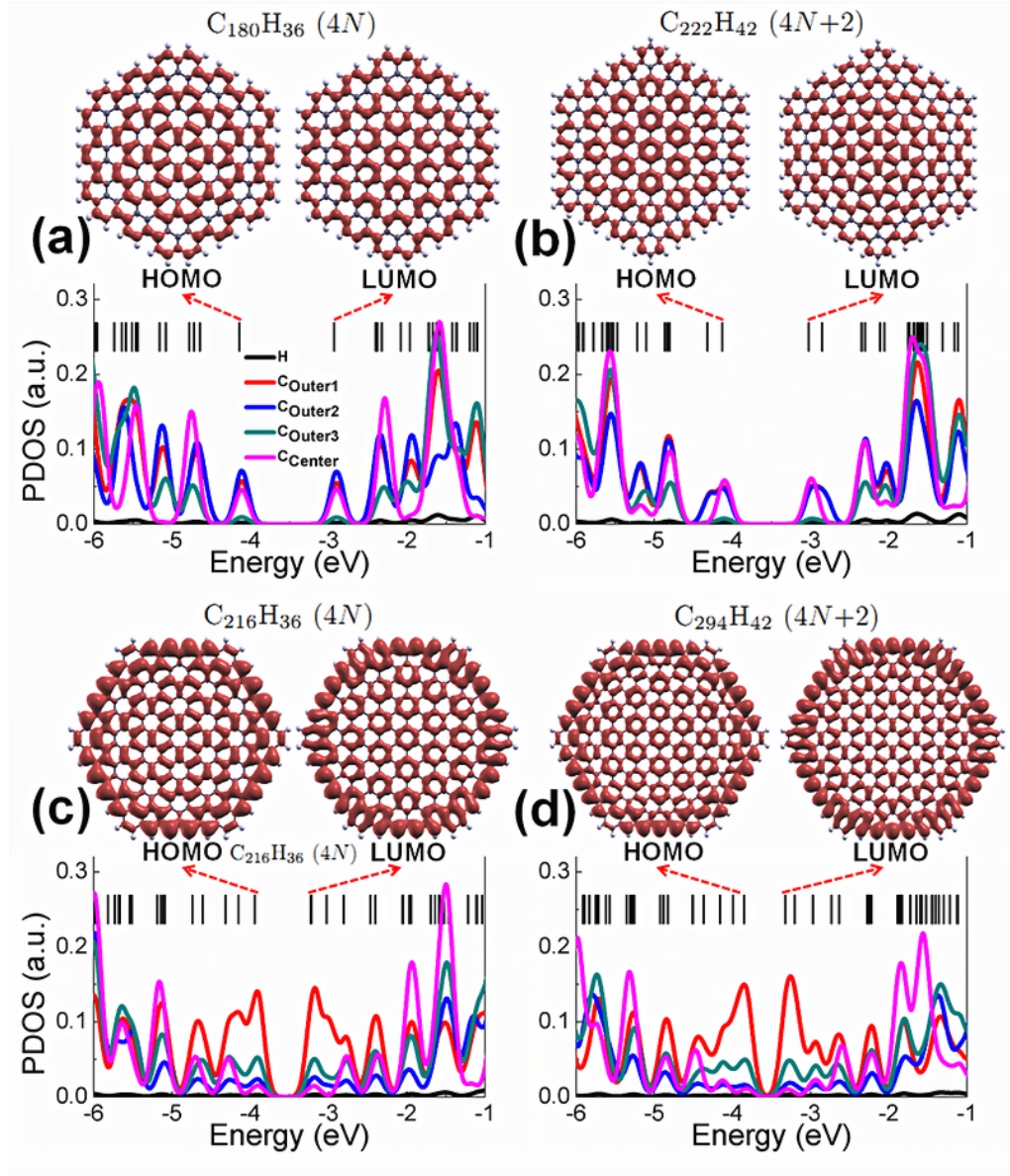


FIG. 6: (Color online) Energy levels and projected density of states (PDOS) of small ACGNFs and ZZGNFs, (a)  $C_{180}H_{36}$  ( $4N$ ), (b)  $C_{222}H_{42}$  ( $4N+2$ ), (c)  $C_{216}H_{36}$  ( $4N$ ) and (d)  $C_{294}H_{42}$  ( $4N+2$ ), including PDOS per atom of hydrogen atoms (H), outermost ( $C_{Outer1}$ ), second outer ( $C_{Outer2}$ ), third outer ( $C_{Outer3}$ ) and central ( $C_{Center}$ ) carbon atoms. Their local density of states (LDOS) of HOMO and LUMO are shown in the insert. Two kinds of delocalized double bonds ( $CH=CH-C=C-CH=CH$  and  $CH-CH=C-C=CH-CH$ ) in outer region of HOMO states in ACGNFs are marked by pink arrows.

of ACGNFs make equal contributions to the HOMO and LUMO energy levels, although the contribution from the third outer layer is significantly smaller than those from first two outer layers. We also observe that hydrogen atoms make negligible contribution.

Interestingly, the  $3n$ th ( $n$  is a small integer) outer layer carbon atoms of ACGNFs, especially in large-scale, have no contribution to their HOMOs and LUMOs. It can be seen from circularly averaged hydrogen projected density of states (PDOS), the outermost, the second and the third outer layer of carbon atoms as well as carbon atoms at the center of the GNF and their correspond-

ing local HOMO and LUMO density of states (LDOS) as shown in Figs. 6, 7 and 8, the third outer layer of carbon atoms in small ACGNFs ( $C_{180}H_{36}$  and  $C_{222}H_{42}$ ) all have no contribution to their HOMOs and LUMOs due to delocalized double bonds formed between the outermost and second outer layer of carbon atoms. For large ACGNFs ( $C_{684}H_{72}$ ,  $C_{762}H_{78}$ ,  $C_{2244}H_{132}$  and  $C_{2382}H_{138}$ ), the third, sixth and even ninth outer carbon atoms also have no contribution to their HOMOs and LUMOs. Furthermore, there is a competition between the delocalized double bonds near the armchair edge carbon atoms and the all-benzenoid or non-benzenoid structure in the inner

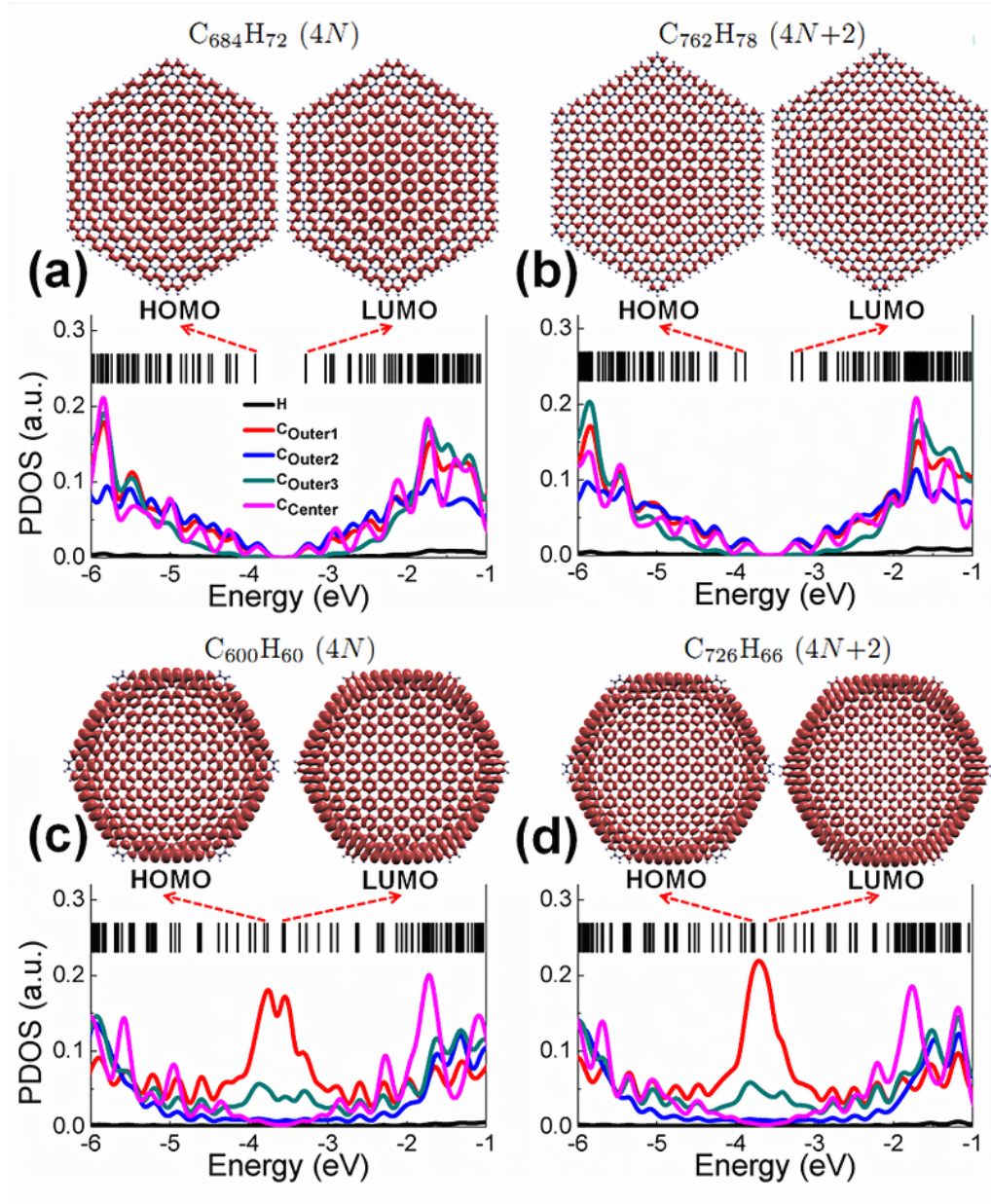


FIG. 7: (Color online) Energy levels and projected density of states (PDOS) of large ACGNFs and ZZGNFs, (a)  $C_{684}H_{72}$  ( $4N$ ), (b)  $C_{762}H_{78}$  ( $4N+2$ ), (c)  $C_{600}H_{60}$  ( $4N$ ) and (d)  $C_{726}H_{66}$  ( $4N+2$ ), including PDOS per atom of hydrogen atoms (H), outermost ( $C_{Outer1}$ ), second outer ( $C_{Outer2}$ ), third outer ( $C_{Outer3}$ ) and central ( $C_{Center}$ ) carbon atoms. Their local density of states (LDOS) of HOMO and LUMO are shown in the insert. Two kinds of delocalized double bonds ( $CH=CH-C=C-CH=CH$  and  $CH-CH=C-C=CH-CH$ ) in outer region of HOMO states in ACGNFs are marked by pink arrows.

region of the HOMO states, as the sizes increase. But, this effect does not exist in ZZGNFs, because rich outer edge states dominate their HOMOs and LUMOs. Furthermore, the third outer layer of carbon atoms even show more contribution to their HOMOs and LUMOs compared with the second outer carbon atoms in ZZGNFs. Therefore, carbon atoms in GNFs show different chemical activity. The difference depends on their sizes, edge types and the total number of electrons.

Fig. 7(a) and (b) show that large ACGNFs, such as

$C_{684}H_{72}$  and  $C_{762}H_{78}$  remain as semiconductors with reduced HOMO-LUMO energy gaps. The estimated HOMO-LUMO gaps are 0.64 eV for  $C_{684}H_{72}$  and 0.60 eV for  $C_{762}H_{78}$ . The DOS and PDOS plots associated with these ACGNFs do not have elevated peaks near the HOMO and LUMO levels. In contrast, large ZZGNFs  $C_{600}H_{60}$  and  $C_{726}H_{66}$  exhibit metallic characteristics, which can be seen from the much higher DOS values near the Fermi level depicted in in Fig. 7(c) and (d). The presence of a peak near the Fermi level is also



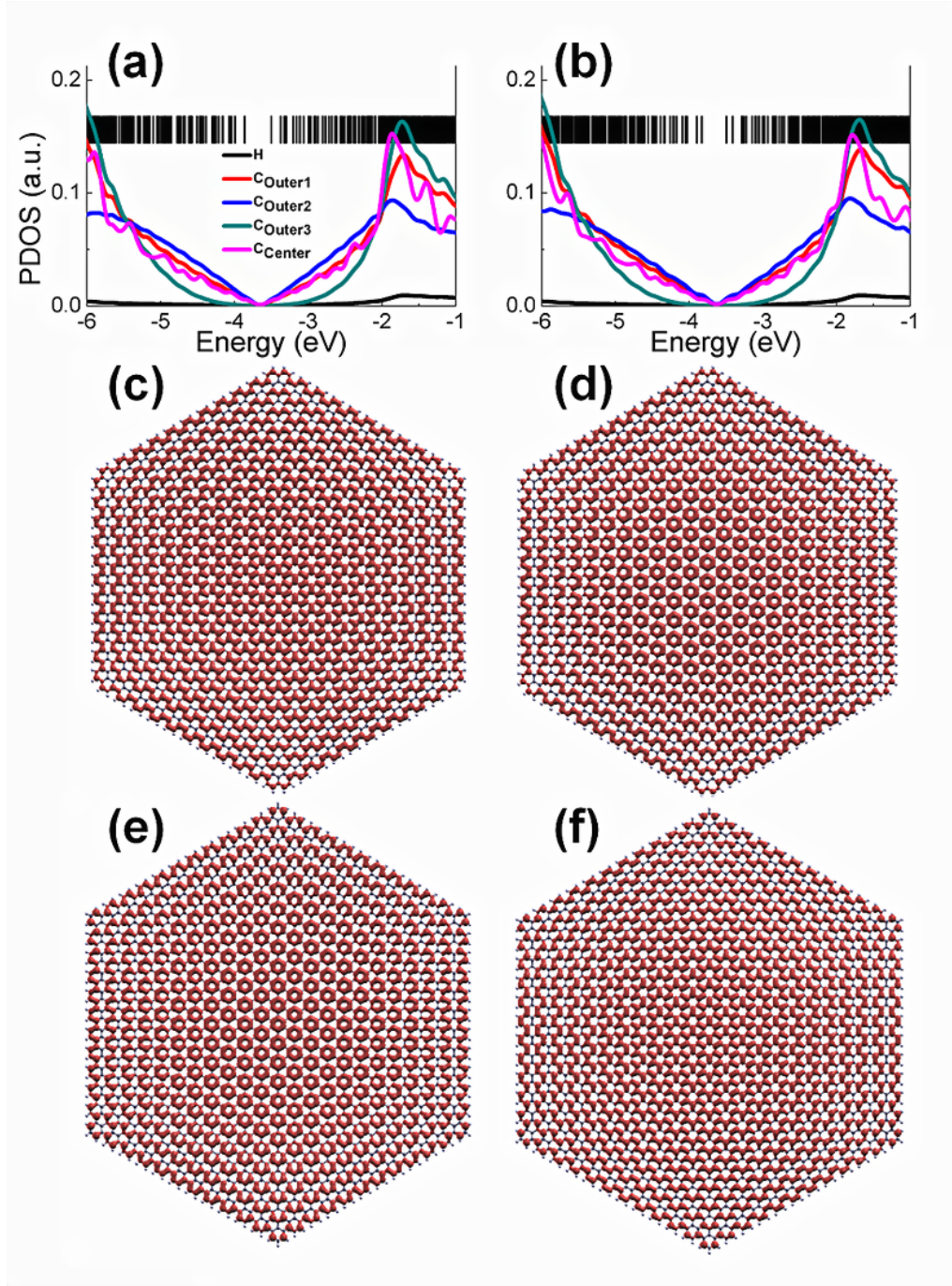


FIG. 8: (Color online) Energy levels and projected density of states (PDOS) of large ACGNFs, (a)  $C_{2244}H_{132}$  ( $4N$ ), (b)  $C_{2382}H_{138}$  ( $4N+2$ ), including PDOS per atom of hydrogen atoms (H), outermost ( $C_{Outer1}$ ), second outer ( $C_{Outer2}$ ), third outer ( $C_{Outer3}$ ) and central ( $C_{Center}$ ) carbon atoms, and their corresponding local density of states (LDOS) of HOMO and LUMO, (c) HOMO of  $C_{2244}H_{132}$ , (d) LUMO of  $C_{2244}H_{132}$ , (e) HOMO of  $C_{2382}H_{138}$  and (f) LUMO of  $C_{2382}H_{138}$ .

correlated with much higher LDOS values on the edges of the large ZZGNFs, which are likely to be contributed by edge states, as we discussed earlier. Furthermore, edge states in ZZGNFs become more localized as the sizes increase, agreeing well with previous tight-binding predictions [33]. Our results suggest that the presence of many edge states tend to make large ZZGNFs thermodynam-

ically unstable, which is also manifested by their relatively high cohesive energy levels compared with those of ACGNFs. Similar conclusions have been reached for GNRs [41–43].



### D. Aromaticity

We observe from the HOMO and LUMO LDOS plots shown in Figs. 6 and 7 that the  $\pi$ -electron distribution patterns in the inner region of ACGNFs and ZZGNFs are different from those in the outer regions of the nanoflakes. In the inner region, the HOMO and LUMO states of ACGNFs and ZZGNFs exhibit distinct aromatic and anti-aromatic characteristics. For example, in the inner region of  $C_{180}H_{36}$ , which is an ACGNF with  $4N$  electrons, the carbon atoms appear to form  $\pi$ -electron Clar sextets in HOMO states shown in Fig 6(a), and empty hexagonal rings can be seen in the inner region of its LUMO states. Both the sextets and empty rings have a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  periodicity. These inner  $\pi$ -electron distribution patterns are similar to those found in GNRs [42].

In the outer region, alternating single and delocalized olefinic double bonds (CH-CH=C-C=CH-CH) can be observed in the HOMO and LUMO LDOS of ACGNFs, whereas the outer region of the ZZGNFs are dominated by edge states.

The aromatic structure in the inner region of an ACGNF depends on whether it has  $4N$  or  $4N + 2$  electrons. ACGNFs with  $4N+2$  electrons belong to all-benzenoid polycyclic aromatic hydrocarbons with aromaticity [32]. We can observe from Fig. 6 (b) that this type of ACGNFs have unique Clar formulas that correspond to all-benzenoid structures with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  periodicity. A similar observation is made in [33] based on a tight-binding model. However, ACGNFs with  $4N$  electrons appears to have non-benzenoid structures that contain empty hexagonal rings with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  periodicity in the inner region of their HOMO states shown in Fig. 6(a).

As we mentioned earlier, the outer regions of ACGNFs consist of alternating single and delocalized olefinic double bonds formed along the armchair edges. However, the locations of the double bonds are different for ACGNFs with  $4N$  electron and those with  $4N+2$  electrons. For ACGNFs with  $4N$  electrons, the bonding pattern can be labeled by CH=CH-C=C-CH=CH, whereas for ACGNFs with  $4N+2$  electrons, the pattern becomes CH-CH=C-C=CH-CH. Thus, the locations of chemical addition reaction associated with ACGNFs with  $4N$  electrons are different from those associated with ACGNFs with  $4N+2$  electrons. Such difference may affect the carrier mobility along the edges of ACGNFs, similar to the effects observed for ACGNRs [17] as well as the stability of the GNF.

Based on the cohesive energy results we presented earlier, we predict that ACGNFs with  $4N$  electrons are slightly more stable than ACGNFs with  $4N+2$  electrons of comparable sizes. This is particularly true for large ACGNFs with thousands of atoms. However, the HOMO LDOS plot shows that ACGNFs with  $4N$  electrons exhibits non-benzenoid structures that contain empty hexagonal rings with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  periodic-

ity, which can be interpreted as a linear combination of two Clar formulas in the inner region. Such a linear combination tends to be less stable than all-benzenoid polycyclic aromatic hydrocarbons (PAHs) with unique Clar formulas observed in ACGNFs with  $4N+2$  electrons as illustrated in Fig. 9. However, the relative stability of a system is determined both by the inner structure and by the boundary structure, which is reflected here by the steric effects of the  $\pi$ -electrons near the boundary and the locations of delocalized olefinic double bonds. The slightly higher stability of ACGNFs with  $4N$  electrons compared to  $4N+2$  electrons indicates the competition between Clar's theory for the inner structure and the steric effects of the boundary structure.

For ZZGNFs, we also observe non-benzenoid or all-benzenoid structures in the inner regions of their HOMO states depending on whether they have  $4N$  or  $4N + 2$  electrons. However, the difference in these inner region aromatic structures appears to have little effect on their cohesive energy. This also indicates the importance of the boundary, which is dominated by the edge states ( $\dot{C}H-C-\dot{C}H-C-\dot{C}H-C$ ) for ZZGNFs.

## IV. SUMMARY AND CONCLUSIONS

In summary, we investigate the effects of the sizes and edges on the stability and electronic structure of hexagonal graphene nanoflakes (GNFs) using first-principle calculations at an unprecedented scale. This is enabled through the recently developed SIESTA-PEXSI method for efficient treatment of large scale electronic structure calculations even for systems of metallic characteristics. The main findings of this paper is given in Table I, summarizing the properties of ACGNFs and ZZGNFs with  $4N$  and  $4N + 2$  electrons, respectively. The results presented in this study are important to the understanding of size and edge dependency of GNFs with potential applications for graphene-based electronic applications at nanoscale.

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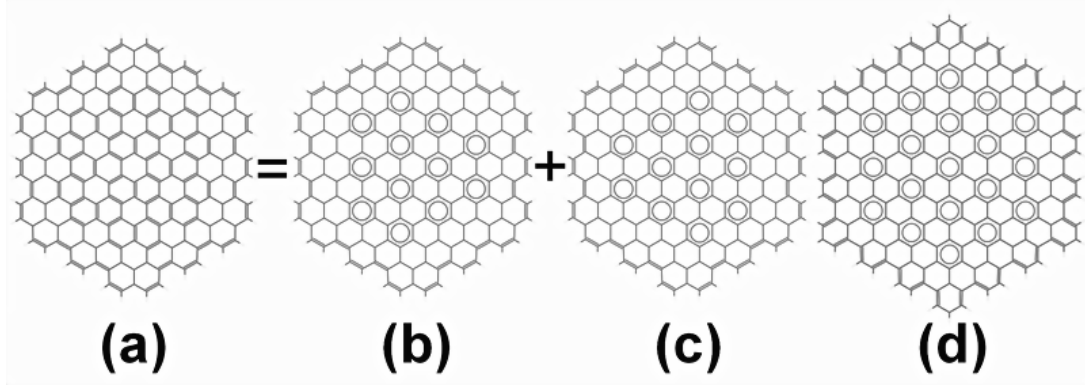


FIG. 9: (Color online) The Kekulé and Clar structure models of ACGNFs, (a) the Kekulé formulas, (b) and (c) two Clar formulas of  $C_{180}H_{36}$  ( $4N$ ), and (d) unique Clar formulas of  $C_{222}H_{42}$  ( $4N+2$ ).

TABLE I: The PEXSI method calculated stability and electronic properties (energy gap, inner and outer HOMO) of large GNFs with different edges (ACGNFs and ZZGNFs) and total number of electrons ( $4N/4N+2$ ,  $N$  is an integer).

GNFs	ACGNFs		ZZGNFs	
Number of electrons	$4N$	$4N+2$	$4N$	$4N+2$
Stability	Most stable	Stable	Unstable	Unstable
	Low chemical reactivity		High chemical reactivity	
Energy gap	$E_g = 3.37/L$		$E_g = -0.62 + 3.97/L$	
	All semiconducting		Metallic for $L > 6.40$ nm	
Inner HOMO	Non-benzenoid	All-benzenoid	Non-benzenoid	All-benzenoid
	Two Clar formulas	Unique Clar formulas	Two Clar formulas	Unique Clar formulas
Outer HOMO	Delocalized double bonds		Rich localized edge states	
	CH=CH-C=C-CH=CH		ĊH-C-ĊH-C-ĊH-C	

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